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REPORT No. 23/R/62

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The Thermal Decomposition of 2-Ethyldecaborane

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³ (REPORT NO. 23/R/62)

⁴ (The Thermal Decomposition of 2-Ethyldecaborane)

by

⁵ (F.W. Emery, ^{+ others} P.L. Harold and A.J. Owen)

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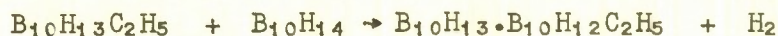
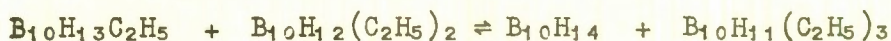
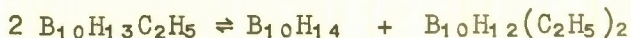
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Reference: WAC/138/022

1. SUMMARY

The kinetics of the thermal decomposition of 2-ethyldecaborane have been investigated for a static system in the temperature range 210° - 230°C and at 2-ethyldecaborane pressures of 100 - 600 mm Hg. The decomposition leads initially to decaborane and diethyldecaboranes; its rate is of the second order with respect to 2-ethyldecaborane; the activation energy is 39.5 ± 0.5 kcal/mole.

In the later stages of the decomposition the reaction deviates from the second order dependence due to side reactions which give nonvolatile solid hydrides, alkylated nonvolatile solid hydrides, hydrogen, methane and a little ethane. The following reaction mechanism has been proposed:



1,2-diethyldecaborane is always present in the products in greater concentration than 2,4-diethyldecaborane. This and other results have been interpreted in terms of a hyperconjugation effect of the alkyl group with the σ B-B bonds in the decaborane structure.

2. INTRODUCTION

2-ethyldecaborane can be obtained by the gas phase reaction of decaborane with ethyl bromide at 230°C (1). The reaction is complex. Yields are lower than the equation



predicts, due to side reactions - for example, the thermal decomposition of decaborane. The present work was concerned with a study of the thermal decomposition of 2-ethyldecaborane, in order to assess its importance in the synthesis process. The decomposition has been investigated in the temperature range 210° - 230°C and a mechanism proposed: several side reactions were also studied at 220°C. The results give interesting indications on the electron distribution in the 2-ethyldecaborane molecule.

Earlier work on the thermal decomposition of 2-ethyldecaborane was concerned with the liquid phase reactions (2,3,4). McDonald (2) found that HEF 3 (mainly 2-ethyldecaborane) was more stable to pyrolysis than pentaborane but less stable than decaborane. Tannenbaum (3) and Raines and Grelecki (4) carried out a more thorough investigation and analysed the products by flash distillation and gas chromatography. They concluded that the initial reaction gave decaborane and diethyldecaborane. 1-Iodo-octane was found to be an inhibitor in the thermal decomposition.

/3.

3. EXPERIMENTAL

3.1 Reactants

2-ethyldecaborane and 1,2 and 2,4-diethyldecaboranes, prepared by a Friedel-Crafts ethylation of decaborane, were separated from the reaction mixture by preparative gas chromatography (5). The sample of 2-ethyldecaborane was shown to be 99 per cent pure by alkaline persulphate oxidation to boric acid (6). Its vapour pressure up to 150°C was measured in a spiral gauge apparatus by a null method; these results are shown as full circles in Figure 1. Other values of the vapour pressure, interpolated from the results of the decomposition experiments of Tannenbaum (3), and the extrapolated boiling point of 220°C recorded by Wise and Lipschitz (7), are shown as crosses in the same graph.

1,2 and 2,4-diethyldecaboranes were incompletely separated by the preparative column; each was shown by gas chromatography to contain about 5 per cent of the other isomer.

Decaborane, m.p. 99.7°C was purified by crystallisation from hexane followed by vacuum sublimation (1).

The scope of the investigation was limited by the availability of the reactants.

3.2 Apparatus

Experiments were carried out in Pyrex reaction vessels previously illustrated (8), having a total volume of ~150 c.c. They consisted of a reaction bulb and an entry tube, 15 cm long, comprising a B.10 cone on the end of a 7-cm stem of a B.14 cone. Liquid reactants were introduced into the weighed reaction vessel of known volume by means of an Agla pipette having an 18-cm hypodermic needle, while the solid decaborane was introduced by means of a funnel which prevented the sides of the entry tube from being contaminated. After weighing, the bulbs were evacuated, sealed and heated in an "Aroclor" bath (1).

Experiments were carried out for varying times at 210°, 220° and 230°C and at initial 2-ethyldecaborane pressures of 100 to 600 mm. A limited number of experiments were carried out at 220°C on the side reactions, e.g. 2-ethyldecaborane with decaborane, diethyldecaborane with decaborane, diethyldecaborane with ethyldecaborane, and the decomposition of diethyldecaborane alone. The products of the reaction were a mixture of polyethyldecaboranes, decaborane, polymerised polyethyldecaborane, nonvolatile solid hydrides and a mixture of hydrogen, methane and a little ethane. Decaborane was occasionally observed as needle-like crystals on the side of the cooled reaction vessel.

3.3 Analysis

The products of the reaction were analysed as follows. The gases were shown by mass spectroscopy to consist of hydrogen and methane, with a trace of ethane. Hydrogen was determined by pressure measurements after expansion of the gas into a known volume, the reaction vessel being immersed in liquid nitrogen. For samples from the later stages of the reaction a correction was made for the vapour pressure of methane at this temperature. Methane was then determined by allowing the reaction vessel to warm up either to carbon dioxide/acetone temperature or to room temperature.

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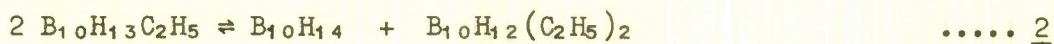
The solid and liquid products were extracted with dry benzene, a known weight of naphthalene added and the composition of the solution quantitatively determined by gas chromatography (9). In all cases, only decaborane, 2-ethyldecaborane and the two diethyldecaboranes were recovered. The higher ethylated decaboranes had large retention volumes and were present in too small a quantity to allow their accurate determination. The solids remaining after benzene extraction were oxidized to boric acid and titrated against baryta (6). This method of analysis gave approximately 95 per cent recovery of the reactant boron; the 5 per cent boron losses have been attributed to the triethyldecaborane and tetra-ethyldecaboranes which are almost certainly formed in the present work and which have been identified in Friedel-Crafts ethylations of decaborane (10).

4. RESULTS AND DISCUSSION

The results are shown in Figures 2 to 5.

4.1 The Course of the Reaction

The course of the thermal decomposition of ethyldecaborane is illustrated in Figure 2 by a set of results which summarises the fate of the 2-ethyldecaborane at 210°C and an initial decaborane pressure of 200 mm. In the initial stages of the reaction hydrogen and methane are not produced, the main products being decaborane and the diethyldecaboranes in the ratio of 2/3 1,2-diethyldecaborane and 1/3 2,4-diethyldecaborane. 2-Ethyldecaborane therefore decomposes according to the equation



It has been written as an equilibrium since 2-ethyldecaborane is a major product of the back reaction of decaborane with diethyldecaborane. At 220°C the ratio of the forward reaction to the back reaction leads to a value of 0.60 for the equilibrium constant for reaction 2.

As the reaction proceeds the yields of diethyldecaborane and of decaborane reach maxima. It will be shown later that these maxima result from the participation of side reactions.

4.2 The Order of Reaction

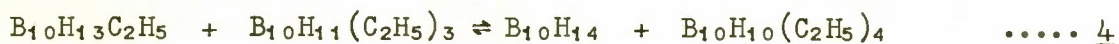
The usual second order graphs of the ratio of 2-ethyldecaborane reacted (x) to that unreacted (a - x) against the product of the initial partial pressure of 2-ethyldecaborane and time of reaction are shown in Figure 3. The plots at each temperature, while falling on a smooth curve, refer to a range of initial pressures of 2-ethyldecaborane, and show that the main reaction of the decomposition is second order. This is in agreement with the conclusion that equation 2 represents the initial step in the decomposition. The values of the rate constants k_1 obtained from the graphs are 6.1×10^{-5} , 1.34×10^{-4} and $2.85 \times 10^{-4} \text{ mm}^{-1} \text{ min}^{-1}$ at temperatures of 210°, 220° and 230°C respectively. Side reactions are responsible for the deviation from the usual second order straight line and also for the formation of the other products.

4.3 Side Reactions

It can be seen in Figure 2 that only 25 per cent of the original carbon of the reacted 2-ethyldecaborane is recovered (either as diethyldecaboranes or as methane). In the early stages of the reaction the percentage is much lower e.g. after 60 minutes reaction time only 12 per cent of the carbon of

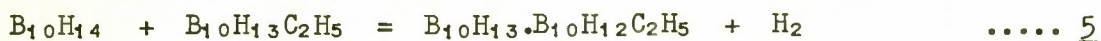
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the 2-ethyldecaborane reacted is recovered as methane. Polyalkylation must therefore occur according to the equations:



the higher ethylated decaboranes decomposing more rapidly than 2-ethyldecaborane. Thus, the experiments carried out at 220°C with 150 mm each of 1,2-diethyldecaborane and 2-ethyldecaborane gave polyethylated decaboranes, the 1,2-diethyldecaborane disappearing more rapidly than the 2-ethyldecaborane. Similar results were observed when 2,4-diethyldecaborane was used instead of the 1,2-derivative. The thermal decomposition of 2,4-diethyldecaborane yielded mainly polyethylated decaboranes and polymerized polyethylated decaborane with a 16 per cent yield of 2-ethyldecaborane. No isomerisation of the 2,4 to 1,2-diethyldecaborane occurred. It is suggested that tetra-ethyldecaborane is the highest ethylated decaborane derivative formed in the reaction, since no higher alkylated derivative has ever been found in Friedel-Crafts alkylation products.

Experiments in which 300 mm of decaborane and 300 mm of 2-ethyldecaborane were heated together at 220°C showed that they react together much more rapidly than would be expected by the thermal decomposition of each compound separately. The gaseous products consist of 95 per cent hydrogen, 4 per cent methane and a little ethane. Presumably the main path of this reaction is a condensation of decaborane with 2-ethyldecaborane in the 1 or 4-position



Hydrogen, besides being formed in the above reaction, is also known to be formed in the thermal decomposition of decaborane (1):



Since B-H bonds are the weakest bonds in ethyldecaboranes (11), hydrogen is likely to be formed by the decomposition of the ethylated nonvolatile solid hydrides.

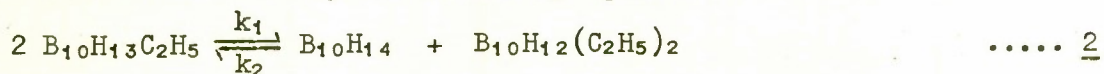
Methane is not found in appreciable quantities until the later stages of the reaction. It must therefore result from a decomposition of the alkylated nonvolatile solid hydrides. The mechanism of methane formation is probably similar to that which occurs in the pyrolysis of ethylbenzene (12), i.e. the side chain splits:



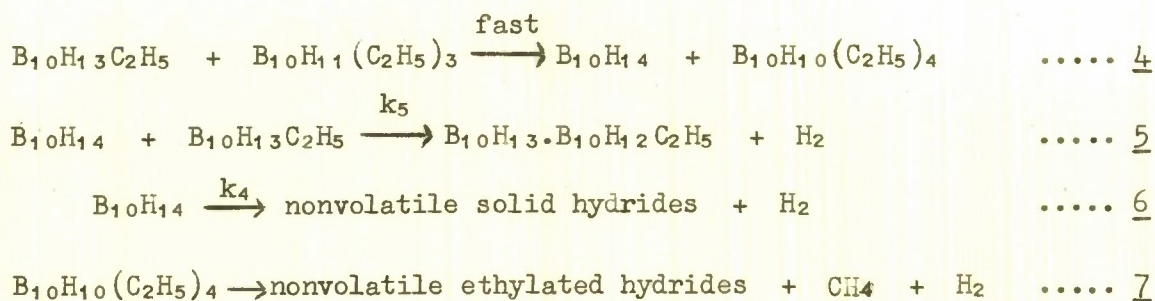
Bond dissociation energies of 89 kcal for the B-C bond and 82.6 kcal for the C-C bond (11) support this view and account for the low yields of ethane.

4.4 The Mechanism

The mechanism of the thermal decomposition of 2-ethyldecaborane may therefore be summarized by the following equations:

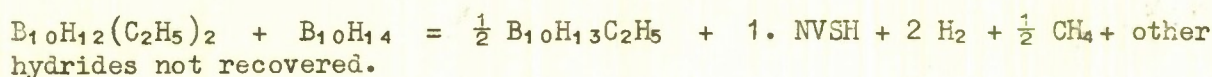


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Calculations of the course of the reaction, using rate constants such that $k_5 \approx k_3 = 25 k_1$, and k_4 values obtained previously (1), lead to the curves drawn in Figure 3 and to the observed maximum yields of decaborane (Fig. 4) and diethyldecaborane. These rate constants are also consistent with the initial rates of disappearance of 2-ethyldecaborane obtained when reactions 3 and 5 were studied independently.

Experiments on the thermal decomposition of diethyldecaboranes have shown that this reaction can be neglected in the present system. Similarly, the back reaction between 1,2-diethyldecaborane and decaborane, which has a rate constant of $2.2 \times 10^{-4} \text{ min}^{-1} \text{ min}^{-1}$, need not be considered. In this case the following stoichiometric equation applies:



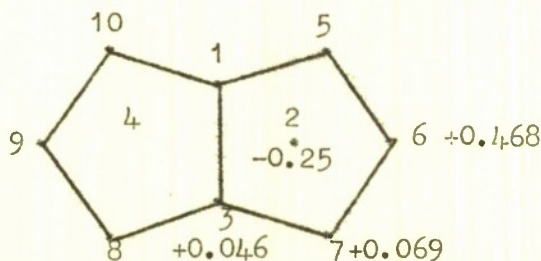
It illustrates the complexity of reactions of this type, showing that many side reactions must occur.

4.5 The Activation Energy

The Arrhenius plot shown in Figure 5 leads to an activation energy of $39.5 \pm 0.5 \text{ kcal/mole}$. This may be compared with the value of 38.8 kcal/mole obtained by Raines and Grelecki (4) during the initial stages of the liquid phase decomposition.

4.6 The Effect of Alkylation on the Electron Distribution in the Decaborane Molecule

Moore, Lohr and Lipscomb (13) have recently recalculated the electronic structure of decaborane by a LCAO method modified by the bridge hydrogens and shown that the electron densities in the molecule are as in I.



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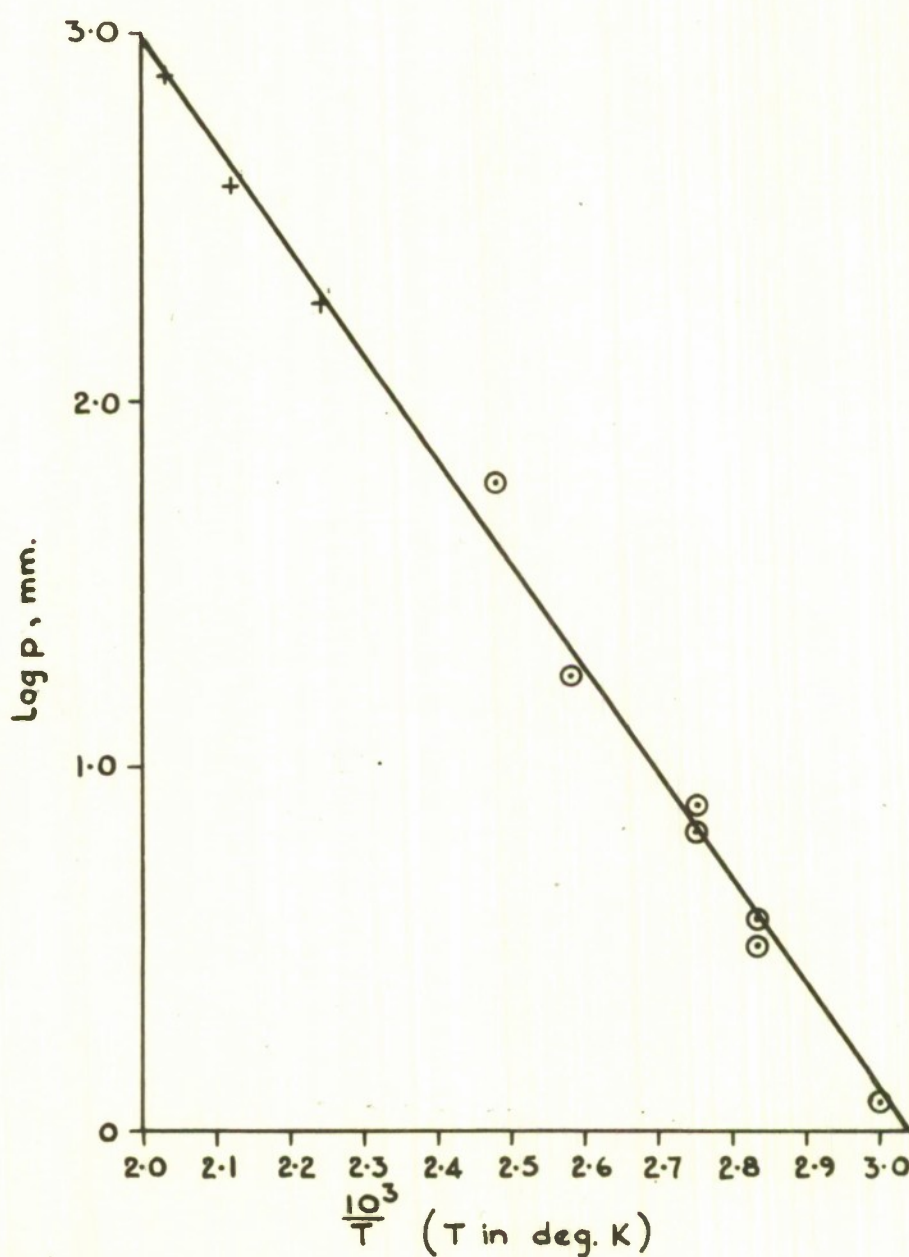
The excess negative charge of 0.8e is contributed by the bridge hydrogen atoms. The calculation predicts the correct order of reactivity of the decaborane ring structure to electrophilic and nucleophilic attack. Thus the reaction of decaborane with ethyl bromide yields initially 2-ethyl-decaborane (1). Further alkylation of 2-ethyldecaborane, however, results in a predominance of 1,2-diethyldecaborane (10). Similar results have been reported in methylation experiments (14); in the present work the ratio of 1,2-diethyldecaborane to 2,4-diethyldecaborane was approximately 2:1. These results suggest that the alkyl group affects the distribution of electrons in the decaborane nucleus. If this were not so 1,2-diethyl-decaboranes would be more reactive than 2,4-dialkyl-decaboranes and in consequence, would be present in much smaller concentrations than 2,4-derivatives. Alkyl substitution (especially in the 2-position) must therefore significantly change the charge distribution in the decaborane molecule. Presumably the alkyl group hyperconjugates with the σ bonds in decaborane and activates the 1,3-positions to an extent that they rival the reactivity of the 4-position. Hyperconjugation effects of this type would also activate the 5,7,8 & 10-positions and would explain the presence of 1,2,3,5(or 8)-tetramethyldecaborane which has been identified in the reaction products of a Friedel-Crafts methylation at 80°C (14).

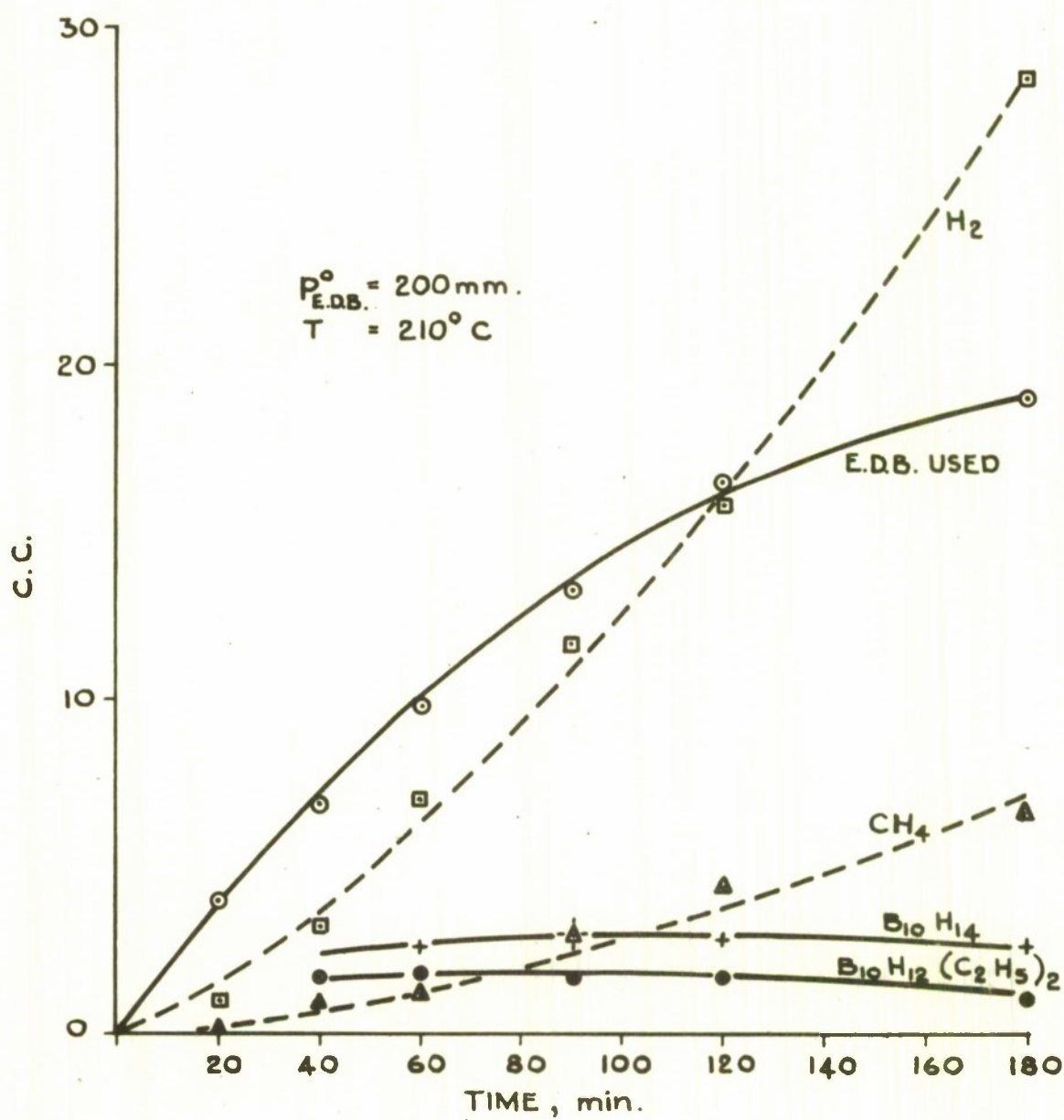
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The authors thank Mr. N.J. Blay and Mrs. P.E. Fuller for the samples of the ethyldecaboranes and for gas chromatography analyses, and Dr. L. Phillips for the mass spectrometer results.

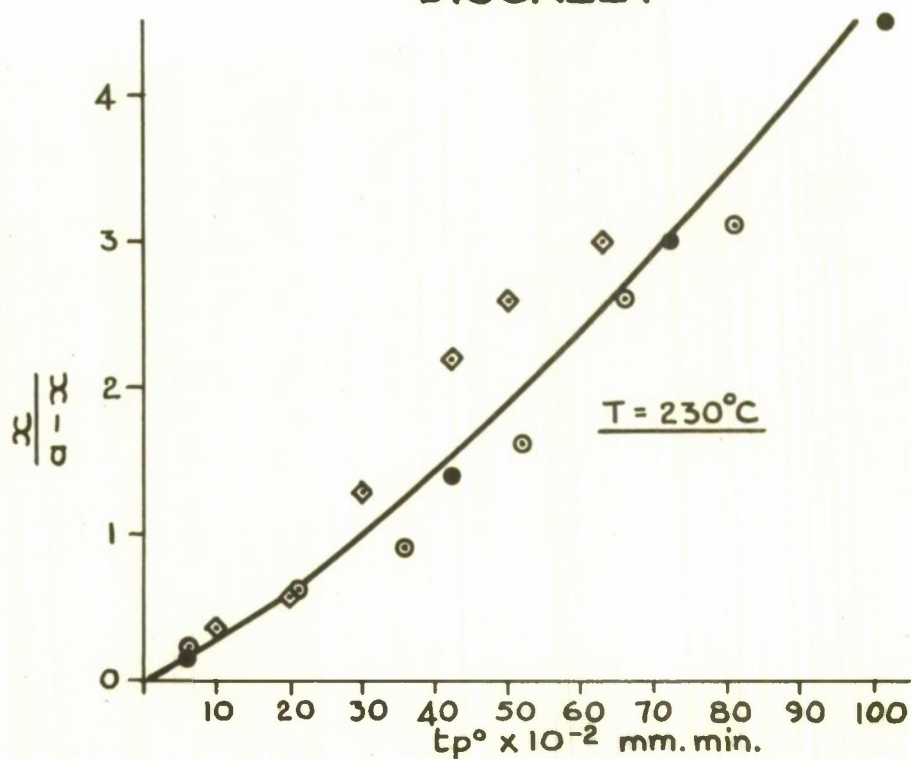
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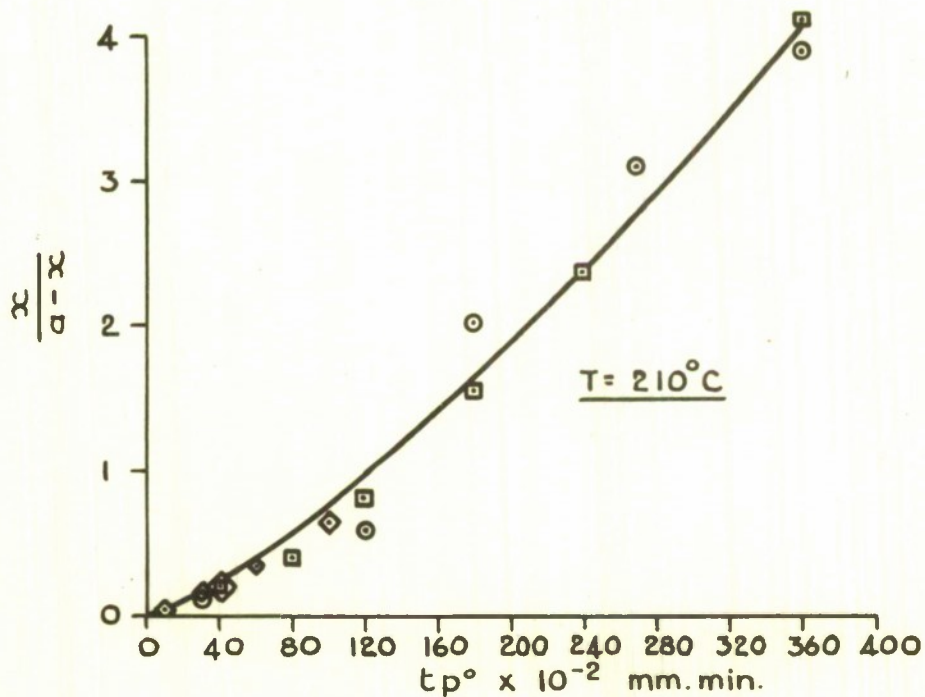
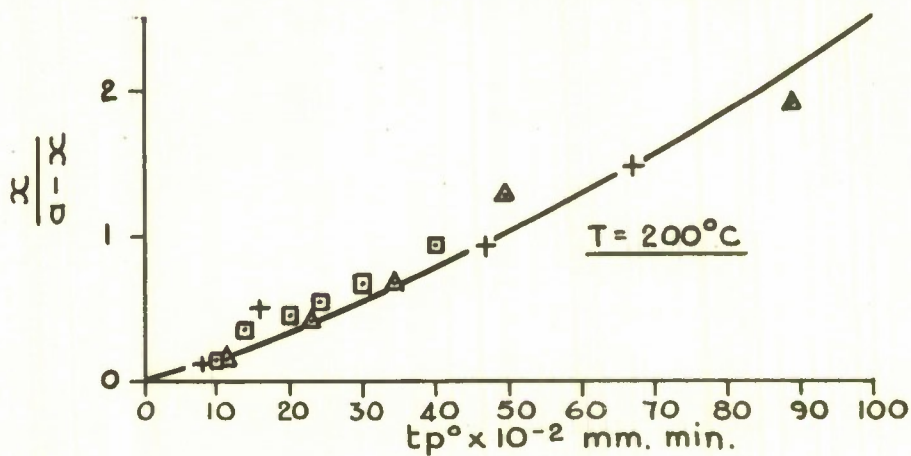
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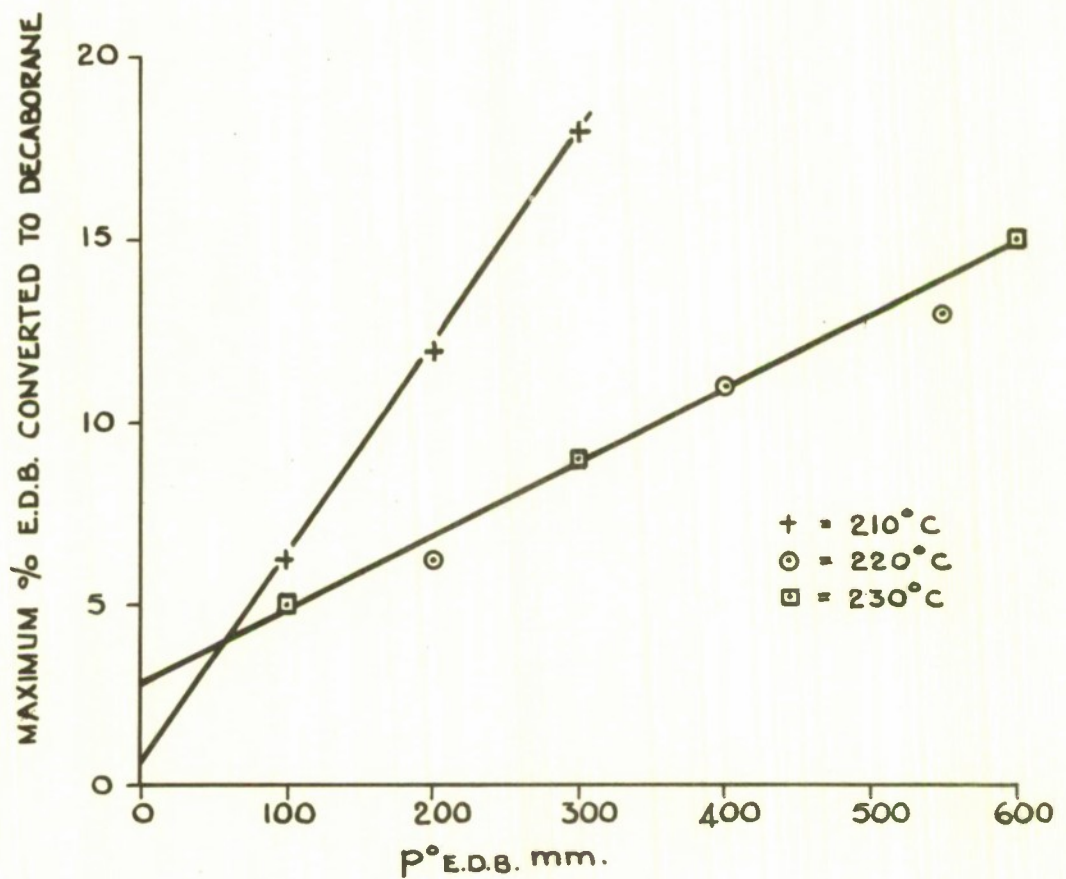
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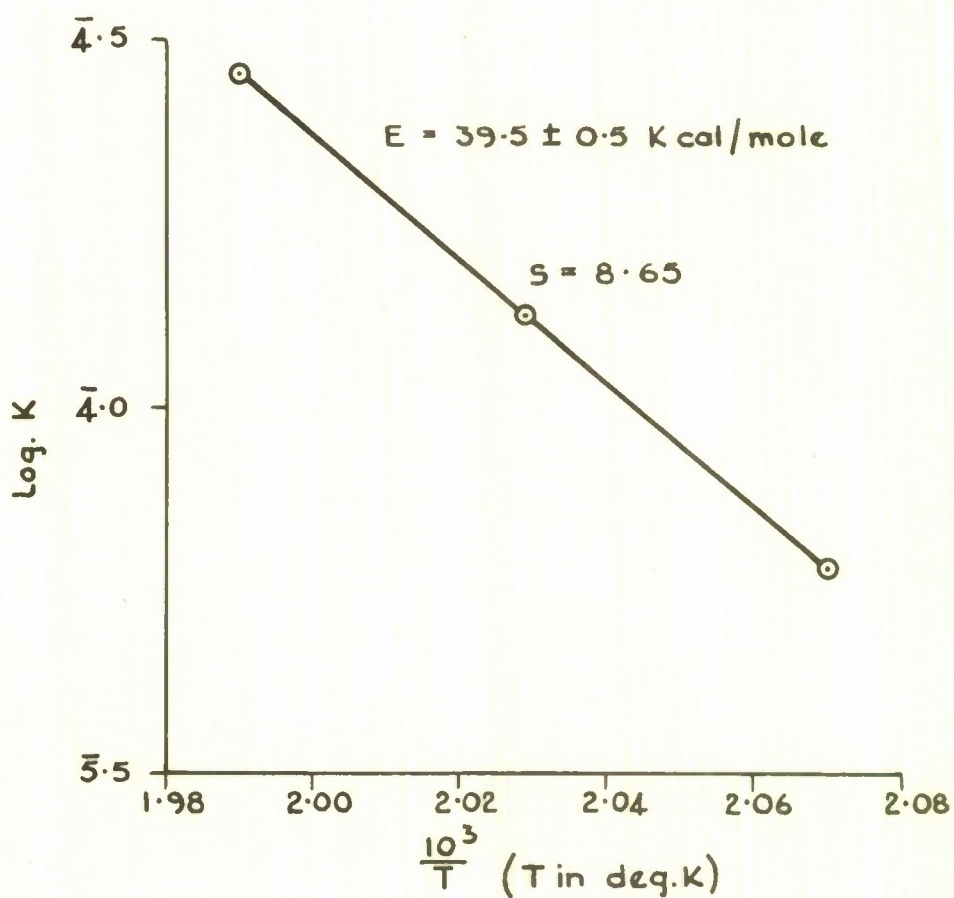


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FIG. 3.

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